

PATENT ABSTRACTS OF JAPAN

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(71)Applicant : NIKKO KYODO CO LTD

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TSUJI MASAHIRO

(54) COPPER ALLOY FOR CONDUCTIVE SPRING

(57)Abstract:

PURPOSE: To obtain a copper alloy having high strength and high conductivity and excellent in stress relaxation property, thermal peeling resistance of plating, silver plating suitability, and stress corrosion cracking resistance.

CONSTITUTION: The alloy is an alloy which has a composition containing 0.5-4.0% Ni, 0.1-1.0% Si, 0.01-0.1% Mg, $\leq 0.0015\%$ S, and $\leq 0.0015\%$ O or further containing, as accessory components, 0.005-1.0% of one or ≥ 2 elements among P, B, As, Fe, Co, Cr, Al, Sn, Ti, Zr, In, and Mn and further an alloy which has a composition containing, besides the above components, 0.01-15% Zn. This alloy can be used for terminal, connector, relay, switch, etc.

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[Date of request for examination] 04.08.1993

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CLAIMS

[Claim(s)]

[Claim 1] nickel: The copper alloy for conductive springs characterized by the bird clapper from Remainder Cu 0.5-4.0% (it is below the same% of the weight), Si:0.1-1.0%, Mg:0.01-0.1%, S:0.0015% or less, and O:0.0015% or less.

[Claim 2] nickel: The copper alloy for conductive springs characterized by the bird clapper from Remainder Cu 0.5-4.0%, Si:0.1-1.0%, Mg:0.01-0.1%, Zn:0.01-15%, S:0.0015% or less, and O:0.0015% or less.

[Claim 3] nickel: 0.5-4.0%, Si:0.1-1.0%, and Mg: — the copper alloy for conductive springs which contains one sort or two sorts or more 0.005 to 1.0% as an accessory constituent further among P, B, As, Fe, Co, Cr, aluminum, Sn, Ti, Zr, In, and Mn, and is characterized by the bird clapper from Remainder Cu O:0.0015% or less S:0.0015% or less 0.01 to 0.1%

[Claim 4] nickel: 0.5-4.0%, Si:0.1-1.0%, Mg:0.01-0.1%, Zn: 0.01-15%, S:0.0015% or less, O:0.0015% or less. The copper alloy for conductive springs which furthermore contains one sort or two sorts or more 0.005 to 1.0% as an accessory constituent among P, B, As, Fe, Co, Cr, aluminum, Sn, Ti, Zr, In, and Mn, and is characterized by the bird clapper from Remainder Cu.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the copper alloy for conductive springs used for a terminal, a connector, a relay, a switch, etc.

[0002]

[Description of the Prior Art] Conventionally, as a copper alloy for these springs, brass and phosphor bronze are used widely and titanium copper and the beryllium copper were used for what high intensity is required as in part.

[0003]

[Problem(s) to be Solved by the Invention] In recent years, what has high intensity and a high spring property is called for by the miniaturization of a device and parts, and a good material of a stress relaxation characteristic is especially called for from a viewpoint of the long-term reliability of a spring property. Moreover, since it is necessary to prevent the temperature rise of the parts at the time of use as much as possible to make a stress relaxation characteristic good, material with high electrical conductivity is called for good [thermolysis nature].

[0004] The heat-resistant detachability of Sn plating and solder plating is still better, and high-reliability material without the migration phenomenon under existence of moisture is called for. To such demand characteristics, although brass is a low cost, it is inferior to intensity and spring nature, and stress corrosion crack sensitivity is also high. Moreover, phosphor bronze and titanium copper had low electrical conductivity, and the beryllium copper is expensive and had merits and demerits, respectively.

[0005] Then, although the alloy of recent years many is shown, since the Cu-nickel-Si system alloy is excellent also with intensity and conductivity also in it, it is observed. Since a stress relaxation characteristic will be further improved if Mg is added as shown especially in USP4594221 (JP,61-250134,A), it is a material suitable as spring material. However, it turns out that the heat-resistant detachability of plating deteriorates remarkably when this alloy adds Mg, and the improvement was called for.

[0006]

[Means for Solving the Problem] As a result of inquiring about a Cu-nickel-Si-Mg system alloy in view of this situation, it came to obtain the alloy with which it is satisfied of many properties of all as spring material.

[0007] this invention Namely, nickel:0.5-4.0%, Si:0.1-1.0%, Mg: 0.01-0.1%, S:0.0015% or less, O:0.0015% or less, To the copper alloy or the above which consists of the remainder Cu, further P, B, As, Fe, They are the copper alloy which contains one sort or two sorts or more 0.005 to 1.0% among Co, Cr, aluminum, Sn, Ti, Zr, In, and Mn, and the alloy for conductive springs further contained Zn:0.01 to 15% into both the above-mentioned alloys, respectively.

[0008] Each reason for component limitation of this invention alloy is shown below. Although nickel generates Si and an intermetallic compound by the aging treatment and the reasons for making nickel content into 0.5 - 4.0% are intensity and a principal component which raises both conductivity, when intensity is low and exceeds 4.0%, they are for processability to fall at less than 0.5%.

[0009] although Si is effective in raising the migration-proof nature other than the effect which raises intensity, without seldom lowering conductivity with nickel, if the reason for making the content into 0.1 - 1.0% does not have those effects at less than 0.1% and exceeds 1.0%, conductivity will fall remarkably -- it is a sake

[0010] Although Mg raises a stress relaxation characteristic, it is a component which degrades the heat-resistant detachability of plating, and when it cannot improve a stress relaxation characteristic even if the reason for making Mg content into 0.01 - 0.1% specifies S and O, but it exceeds 0.1%, it is for the heat-resistant detachability of plating to fall at less than 0.01%.

[0011] The reason for making S content into 0.0015% or less In order to also make a stress relaxation characteristic good further, making Mg content low and improving the heat-resistant detachability of plating If it is because it turns out that S content does very important influence and S exists exceeding 0.0015% It is for Mg to serve as a sulfide so much and to distribute in material, to permeate, if a stress relaxation characteristic is not not only improved, but a plating article is heated while the heat-resistant detachability of plating deteriorates, even if Mg content is low, and for the defect of a blister to come to occur. The reason for making O content into 0.0015% or less is also to permeate, if a plating article is heated while a stress relaxation characteristic is not not only improving, but being completely the same as that of S, Mg's serving as an oxide and the heat-resistant detachability of plating deteriorating, and for the defect of a blister to occur.

[0012] That is, even if it begins by making both the contents of S and O into 0.0015% or less and makes Mg content low, the stress relaxation characteristic has been improved and the heat-resistant detachability of plating can be improved by making it low.

[0013] It became clear that a convention of the content of S and O is a key point for still a small amount of Mg to also prevent the heat-resistant detachability of plating and the stain of plating, and a blister.

[0014] Although addition of an accessory constituent improves intensity, the reason for making the content of the accessory constituent of P, B, and others into 0.005 - 1.0% is for conductivity to fall remarkably at less than 0.005% while processability will fall, if the effect does not exist and it exceeds 1.0%.

[0015] Although its migration-proof nature improves and it also reduces cost while its heat-resistant detachability of plating improves by adding Zn, when the reason for making Zn content into 0.01 - 15% does not have the effect and it exceeds 15%, it is

because stress corrosion crack sensitivity becomes high rapidly at less than 0.01%.

[0016]

[Example] Next, an example and the example of comparison are explained. Table 1 is component composition of the copper alloy which examined. Dissolution casting of the copper alloy of these composition was carried out in the atmosphere, and the ingot of the size of 30mmx60mmx120mm was obtained. After carrying out 3mm facing of these ingots of one side and removing surface discontinuity mechanically, the thickness of 6mmt(s) was made with rolling between 2-hour heating post heating at the temperature of 800-950 degrees C. After carrying out pickling and removing a surface scale, it cold-rolled by Mr. Atsushi of 0.5mmt. Water quenching after solution treatment was performed for 5 - 10 minutes at the temperature of 800-900 degrees C after that. In addition, the grain size number after this solution treatment was adjusted to 10 micrometers. And after finishing cold-rolling to 0.3mmt(s), it carried out on the conditions from which the maximum intensity is obtained in the aging treatment of 1 - 7 hours at the temperature of 400-500 degrees C, and surface polish was carried out with #1200 emery paper, and the last removed the surface discontinuity of a scale etc. and was taken as the test specimen.

[0017]

[Table 1]

| | | 化 学 組 成 (重量%) | | | | | | | 副成分 |
|-----------------------|----|---------------|------|------|-------|--------|--------|------|--------------------------|
| | | Cu | N i | S i | M g | S | O | Z n | |
| 本 発 明 合 金 | 1 | 残 | 2.25 | 0.55 | 0.026 | 0.0008 | 0.0007 | — | — |
| | 2 | 残 | 3.67 | 0.97 | 0.047 | 0.0010 | 0.0008 | — | Co : 0.23 |
| | 3 | 残 | 1.87 | 0.43 | 0.028 | 0.0010 | 0.0014 | — | Cr : 0.12, Zr : 0.09 |
| | 4 | 残 | 2.71 | 0.60 | 0.098 | 0.0004 | 0.0007 | — | Ti : 0.27, Al : 0.65 |
| | 5 | 残 | 3.50 | 0.80 | 0.049 | 0.0012 | 0.0012 | — | Sn : 0.35, P : 0.007 |
| | 6 | 残 | 0.84 | 0.19 | 0.050 | 0.0012 | 0.0014 | 7.30 | B : 0.008, Al : 0.60 |
| | 7 | 残 | 3.62 | 0.93 | 0.049 | 0.0011 | 0.0005 | 0.92 | — |
| | 8 | 残 | 1.41 | 0.35 | 0.085 | 0.0010 | 0.0013 | 9.80 | Fe : 0.34, Ti : 0.06 |
| | 9 | 残 | 2.85 | 0.75 | 0.067 | 0.0008 | 0.0006 | 1.82 | — |
| | 10 | 残 | 2.51 | 0.61 | 0.038 | 0.0011 | 0.0013 | 0.37 | In : 0.08, As : 0.007 |
| | 11 | 残 | 1.29 | 0.33 | 0.022 | 0.0005 | 0.0009 | 3.16 | Mn : 0.51 |

| | | | | | | | | | |
|------------------|----|---|------|------|-------|--------|--------|------|-------------------------|
| 比 較 合 金 | 12 | 残 | 5.38 | 0.86 | 0.054 | 0.0007 | 0.0009 | — | — |
| | 13 | 残 | 3.10 | 1.13 | 0.092 | 0.0073 | 0.0013 | 1.54 | — |
| | 14 | 残 | 3.19 | 0.75 | 0.003 | 0.0005 | 0.0005 | 18.9 | Sn : 0.53, P : 0.024 |
| | 15 | 残 | 2.54 | 0.68 | 0.33 | 0.0006 | 0.0012 | 5.10 | — |
| | 16 | 残 | 0.38 | 0.12 | 0.015 | 0.0009 | 0.0026 | — | Cr : 0.13 |
| | 17 | 残 | 0.44 | 0.38 | 0.46 | 0.0012 | 0.0014 | — | Fe : 0.16, P : 0.031 |
| | 18 | 残 | 1.96 | 0.45 | 0.051 | 0.0025 | 0.0013 | 26.8 | — |
| | 19 | 残 | 2.89 | 0.69 | — | 0.0011 | 0.0014 | 7.43 | — |
| | 20 | 残 | 1.93 | 0.52 | 0.038 | 0.0032 | 0.0019 | 1.15 | Sn : 2.32 |
| | 21 | 残 | 1.40 | 0.08 | 0.076 | 0.0006 | 0.0008 | 1.42 | — |

[0018] Tensile strength, elongation, conductivity, a stress relaxation characteristic, tinning heatproof detachability, silver plating nature, and stress-corrosion-cracking-proof nature were examined about the test specimen. Tensile strength and elongation measured by performing a tension test using the JIS13B test piece for tensile test. Conductivity measured electric resistance at 20 degrees C by the four probe method after processing to the 10mmwx100ml test piece, and converted it into conductivity. a stress relaxation characteristic -- drawing 1 -- like -- ten -- mmw(s) -- x -- 100 -- mml -- having processed it -- board thickness -- 0.3 -- mm -- a test piece -- the gage length -- l -- = -- 50 -- mm -- height -- y -- zero -- = -- 20 -- mm -- bending stress -- a load -- carrying out -- 150 -- degree C -- 1000 -- an hour -- heating -- the back -- drawing 2 -- being shown -- permanent deformation -- an amount (height) -- y -- measuring -- stress relaxation -- a rate -- [-- [-- After tinning heatproof detachability performs 0.5-0.8-micrometer copper ground plating to a test specimen, Predetermined-time (every 100 hours) heating is carried out at 150 degrees C after cutting to 10mmwx100mml about the thing which electroplated 1-1.5-micrometer tin and which carried out afterbaking reflow processing. 90-degree bending of one side was performed one round trip by 0.3mm (= board thickness) of bend radii, it observed near the bending section on the rear face of front with the visual field of being 20 times many as this, and the existence of plating exfoliation was checked. Silver plating nature measured [what / performed 1 micrometer of silver plating to the test specimen by making copper flash plate plating into a ground] the number of blisters about the field of 2 (7mm**x30 piece) 1470mm after heating for 2 minutes at 450 degrees C. Fixing the test specimen processed into 12.5mmwx150mml in the shape of a loop, indoors, after 12-hour neglect, stress-corrosion-cracking-proof nature was left in the desiccator with a capacity of 10l. which contains 2l. of aqueous ammonia 14%, broke visually, investigated the existence of generating, and evaluated it in time to crack generating. Migration-proof nature processed the test specimen into 10mmwx100mml, set it by 2 sets [1] like drawing 3 , and was immersed into tap water (300ml) like drawing 4 . Next, the direct current voltage of 14V was impressed between the test specimens of these two sheets, and change of the current value to elapsed time was measured. The example of representation of this result is shown in drawing 5 . And evaluation of migration-proof nature was performed in time (the drawing 5 Nakaya mark) until current value is set to 1.0A. These evaluation results are shown in Table 2.

[0019]

[Table 2]

| | | 引張強 さ(N/ mm ²) | 伸び (%) | 導電 率(%) IACS | 応力 緩和 率 (%) | 銅めっ き耐熱 剥離性 (hr) | 銀めっき 性(ふく れの数) | 耐応力 腐食割 れ性 (hr) | 耐マイグ レーショ ン性 (min) |
|----------|----|----------------------------------|-----------|--------------------|----------------------|---------------------------|----------------------|--------------------------|-----------------------------|
| 比較 合金 | 1 | 683 | 7.9 | 49 | 16 | 600 | 0 | > 500 | 530 |
| | 2 | 741 | 5.3 | 41 | 15 | 500 | 0 | > 500 | 700 |
| | 3 | 675 | 8.9 | 49 | 16 | 700 | 0 | > 500 | 500 |
| | 4 | 717 | 6.3 | 42 | 10 | 600 | 0 | > 500 | 570 |
| | 5 | 724 | 5.2 | 37 | 15 | 500 | 0 | > 500 | 620 |
| | 6 | 534 | 13.3 | 40 | 16 | >1000 | 0 | 400 | 420 |
| | 7 | 716 | 6.5 | 45 | 14 | >1000 | 0 | > 500 | 720 |
| | 8 | 642 | 5.2 | 42 | 13 | >1000 | 0 | 400 | 600 |
| | 9 | 698 | 8.4 | 43 | 14 | >1000 | 0 | > 500 | 640 |
| | 10 | 698 | 7.8 | 45 | 16 | >1000 | 0 | > 500 | 570 |
| | 11 | 611 | 11.1 | 42 | 17 | >1000 | 0 | > 500 | 500 |
| 比較 合金 | 12 | 836 | 2.1 | 39 | 15 | >1000 | 0 | > 500 | 680 |
| | 13 | 704 | 6.6 | 29 | 21 | 100 | 67 | > 500 | 830 |
| | 14 | 735 | 4.4 | 23 | 24 | >1000 | 0 | 50 | 790 |
| | 15 | 691 | 4.6 | 41 | 9 | 100 | 0 | 400 | 690 |
| | 16 | 454 | 17.6 | 60 | 22 | 300 | 4 | > 500 | 350 |
| | 17 | 643 | 10.2 | 53 | 10 | 100 | 0 | > 500 | 470 |
| | 18 | 657 | 9.3 | 19 | 21 | >1000 | 3 | 10 | 800 |
| | 19 | 698 | 6.1 | 43 | 23 | >1000 | 0 | > 500 | 670 |
| | 20 | 729 | 5.9 | 37 | 24 | 400 | 10 | > 500 | 520 |
| | 21 | 480 | 22.8 | 52 | 11 | >1000 | 0 | > 500 | 200 |

[0020] It turns out that this invention alloy has good intensity and conductivity from this table, a stress relaxation characteristic is also good, and surface quality, such as tinning heatproof detachability and silver plating nature, is also very good, and stress-corrosion-cracking-proof nature is also good.

[0021] It is contrary to these, and about a comparison alloy, since No.12 have the high amount of nickel, although intensity is high, its elongation is low, and its processability is not so good. Since No.13 have the amount of Si, and the high amount of S, conductivity is low, a stress relaxation characteristic is also bad and surface quality, such as tinning heatproof detachability and silver plating nature, is bad. No.14 have the low amount of Mg, although it is an example with many amounts of Zn, for a low reason, the amount of Mg of a stress relaxation characteristic is not so good, since there are many amounts of Zn, conductivity is low, and stress-corrosion-cracking-proof nature is also bad. No. — although 15 and 17 are examples with many amounts of Mg, and the stress relaxation characteristic is good, tinning heatproof detachability is bad Since the amount of nickel is low and No.16 have zero (oxygen) high amount, sufficient intensity is not obtained but a stress relaxation characteristic, tinning heatproof detachability, and its silver plating nature are bad.

[0022] Since No.18 have many amounts of S, and amounts of Zn, a stress relaxation characteristic, silver plating nature, and its stress-corrosion-cracking-proof nature are bad. Although No.19 are the example which does not add Mg, its a stress relaxation characteristic is not so good.

[0023] Since No.20 have O and the high amount of S, a stress relaxation characteristic, tinning heatproof detachability, and its silver plating nature are bad. Since No.21 have few amounts of Si, sufficient intensity is not obtained but its migration-proof nature is also bad.

[0024] As explained above, this invention alloy O of a Cu-nickel-Si-Mg system alloy, Moreover, a stress relaxation characteristic is also good at high intensity and high electric conduction by specifying the amount of S, adding Zn and adding one sort or two sorts or more in P, B, As, Fe, Co, Cr, aluminum, Sn, Ti, Zr, In, and Mn further. Plating heatproof detachability and silver plating nature are also good, and stress-corrosion-cracking-proof nature is also good.

[0025]

[Effect of the Invention] this invention alloy is a copper alloy with good stress relaxation characteristic, plating heatproof detachability, silver plating nature, and stress-corrosion-cracking-proof nature in high intensity and high electric conduction, and a connector, a relay, a switch, etc. are the copper alloys which should be widely used in an electronic-parts field.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is explanatory drawing of the stress relaxation characteristic examining method.

[Drawing 2] It is explanatory drawing about the amount of permanent deformation of a stress relaxation characteristic examination.

[Drawing 3] It is explanatory drawing of a migration-proof sex-test test specimen.

[Drawing 4] It is explanatory drawing of the migration-proof sex test.

[Drawing 5] It is the graph which shows the current-value field change to the elapsed time in the migration-proof sex test.

[Translation done.]

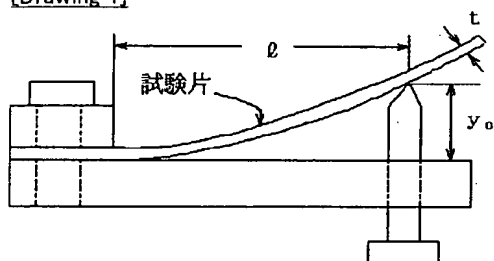
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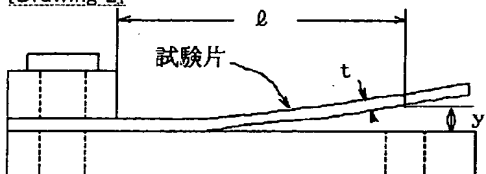
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DRAWINGS

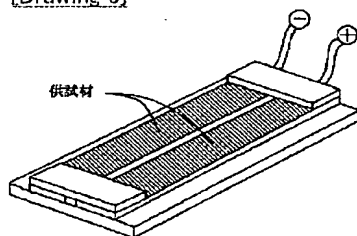
[Drawing 1]



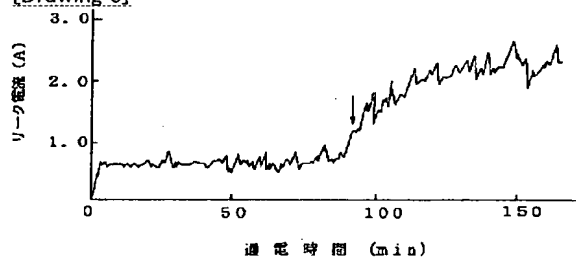
[Drawing 2]



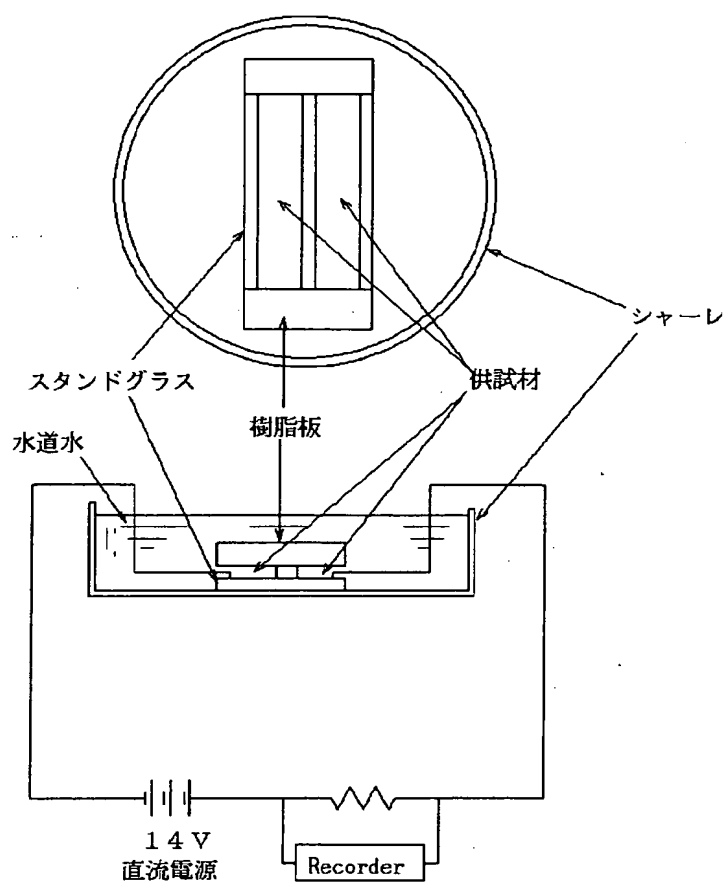
[Drawing 3]



[Drawing 5]



[Drawing 4]



[Translation done.]

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PURPOSE: To obtain a copper alloy having high strength and high conductivity and excellent in stress relaxation property, thermal peeling resistance of plating, silver plating suitability, and stress corrosion cracking resistance. CONSTITUTION: The alloy is an alloy which has a composition containing 0.5-4.0% Ni, 0.1-1.0% Si, 0.01-0.1% Mg, \leq 0.0015% S, and \leq 0.0015% O or further containing, as accessory components, 0.005-1.0% of one or \geq 2 elements among P, B, As, Fe, Co, Cr, Al, Sn, Ti, Zr, In, and Mn and further an alloy which has a composition containing, besides the above components, 0.01-15% Zn. This alloy can be used for terminal, connector, relay, switch, etc.

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(74)代理人 弁理士 小松 秀岳 (外2名)

(54)【発明の名称】 導電性ばね用銅合金

(57)【要約】

【目的】 端子、コネクタ、リレー、スイッチ等に用いられる導電性ばね用銅合金に関する。

【構成】 Ni:0.5~4.0%、Si:0.1~1.0%、Mg:0.01~0.1%、S:0.0015%以下、O:0.0015%以下、あるいはさらに副成分としてP、B、As、Fe、Co、Cr、Al、Sn、Ti、Zr、In、Mnの1種又は2種以上を0.005~1.0%を含有するもの、さらには上記のそれぞれにZn:0.01~15%含有する合金である。

【効果】 高強度、高導電で、応力緩和特性、めっき耐熱剥離性、銀めっき性、対応力腐食割れ性が良好な銅合金である。

【特許請求の範囲】

【請求項1】 Ni:0.5~4.0% (重量%、以下同じ)、Si:0.1~1.0%、Mg:0.01~0.1%、S:0.0015%以下、O:0.0015%以下、残部Cuからなることを特徴とする導電性ばね用銅合金。

【請求項2】 Ni:0.5~4.0%、Si:0.1~1.0%、Mg:0.01~0.1%、Zn:0.01~15%、S:0.0015%以下、O:0.0015%以下、残部Cuからなることを特徴とする導電性ばね用銅合金。

【請求項3】 Ni:0.5~4.0%、Si:0.1~1.0%、Mg:0.01~0.1%、S:0.0015%以下、O:0.0015%以下、さらに副成分としてP、B、As、Fe、Co、Cr、Al、Sn、Ti、Zr、In、Mnのうち1種又は2種以上を0.005~1.0%含有し、残部Cuからなることを特徴とする導電性ばね用銅合金。

【請求項4】 Ni:0.5~4.0%、Si:0.1~1.0%、Mg:0.01~0.1%、Zn:0.01~15%、S:0.0015%以下、O:0.0015%以下、さらに副成分としてP、B、As、Fe、Co、Cr、Al、Sn、Ti、Zr、In、Mnのうち1種又は2種以上を0.005~1.0%含有し、残部Cuからなることを特徴とする導電性ばね用銅合金。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は端子、コネクタ、リレー、スイッチ等に用いられる導電性ばね用銅合金に関するものである。

【0002】

【従来の技術】 従来、これらばね用銅合金としては、黄銅、りん青銅が広く用いられており、一部高強度が要求されるものにはチタン銅、ベリリウム銅が用いられていた。

【0003】

【発明が解決しようとする課題】 近年、機器、部品の小型化により、強度、ばね特性の高いものが求められており、特にばね特性の長期信頼性という観点からは応力緩和特性の良好な材料が求められている。又、応力緩和特性を良好にするには使用時の部品の温度上昇を極力防ぐ必要があるため、放熱性の良好な、即ち電気伝導度の高い材料が求められている。

【0004】 さらにSnめっき、はんだめっきの耐熱剥離性が良好であり、又水分の存在下におけるマイグレーション現象のない高信頼性材料が求められている。これらの要求特性に対し、黄銅は低コストだが強度、ばね性に劣っており、応力腐食割れ感受性も高い。又、りん青銅、チタン銅は電気伝導度が低く、ベリリウム銅は高価であり、それぞれ一長一短があった。

【0005】 そこで、近年多くの合金が提示されているが、中でもCu-Ni-Si系合金が強度、導電性とも優れているため注目されている。特にUSP4594221 (特開昭61-250134) に示されているように、Mgを添加すると応力緩和特性がさらに改善されるため、ばね材として好適な材料である。しかし、本合金はMgを添加することにより、めっきの耐熱剥離性が著しく劣化することがわかっており、改善が求められていた。

【0006】

【課題を解決するための手段】 かかる状況に鑑み、Cu-Ni-Si-Mg系合金について研究を行った結果、ばね材として全ての諸特性を満足する合金を得るに至った。

【0007】 すなわち、本発明は、Ni:0.5~4.0%、Si:0.1~1.0%、Mg:0.01~0.1%、S:0.0015%以下、O:0.0015%以下、残部Cuからなる銅合金あるいは上記にさらにP、B、As、Fe、Co、Cr、Al、Sn、Ti、Zr、In、Mnのうち1種又は2種以上を0.005~1.0%含有する銅合金、さらには上記両合金にそれぞれさらにZn:0.01~15%含有する導電性ばね用銅合金である。

【0008】 本発明合金の各成分限定理由を以下に示す。Ni含有量を0.5~4.0%とする理由は、Niは時効処理によりSiと金属間化合物を生成し、強度、導電性をともに向上させる主成分であるが、0.5%未満では強度が低く、4.0%を超えると加工性が低下するためである。

【0009】 SiはNiとともにあまり導電性を下げずに強度を向上させる効果の他に、耐マイグレーション性を向上させる効果があるが、その含有量を0.1~1.0%とする理由は、0.1%未満ではそれらの効果がなく、1.0%を超えると導電性が著しく低下するためである。

【0010】 Mg含有量を0.01~0.1%とする理由は、Mgは応力緩和特性を向上させるが、めっきの耐熱剥離性を劣化させる成分であり、0.01%未満ではS、Oを規定しても応力緩和特性を改善する事ができず、0.1%を超えるとめっきの耐熱剥離性が低下するためである。

【0011】 S含有量を0.0015%以下とする理由は、Mg含有量を低くし、めっきの耐熱剥離性を改善しながら、さらに応力緩和特性も良好にするには、S含有量が非常に重要な影響を及ぼすことがわかったためであり、Sが0.0015%を超えて存在すると、Mgが多量に硫化物となって材料中に分散され、応力緩和特性が改善されないばかりでなく、Mg含有量が低くてもめっきの耐熱剥離性が劣化するとともに、めっき品を加熱するとし、ふくれといった不良が発生するようになるた

めである。O含有量を0.0015%以下とする理由も、Sとまったく同様であり、Mgが酸化物となり、応力緩和特性が改善されないばかりでなく、めっきの耐熱剥離性が劣化するとともに、めっき品を加熱するとしみ、ふくれといった不良が発生するためである。

【0012】すなわち、S、Oの含有量をともに0.0015%以下とする事により始めてMg含有量を低くしても応力緩和特性を改善でき、かつ低くする事によりめっきの耐熱剥離性を改善できることとなった。

【0013】さらには少量のMgでもめっきの耐熱剥離性並びにめっきのしみ、ふくれを防止するにはS、Oの含有量の規定がキーポイントである事が判明した。

【0014】P、Bその他の副成分の含有量を0.005~1.0%とする理由は、副成分の添加は強度を改善するが、0.005%未満ではその効果がなく、1.0%を超えると加工性が低下するとともに導電性が著しく低下するためである。

【0015】Zn含有量を0.01~15%とする理由は、Znを添加することにより、めっきの耐熱剥離性が向上するとともに耐マイグレーション性が向上し、コストも低減していくが、0.01%未満ではその効果がな

く、15%を超えると応力腐食割れ感受性が急激に高くなるためである。

【0016】

【実施例】次に実施例並びに比較例について説明する。表1は試験をした銅合金の成分組成である。これらの組成の銅合金を大気中で溶解鑄造し、30mm t×60mm w×120mm lの大きさのインゴットを得た。これらのインゴットを片面3mm面削し表面欠陥を機械的に除去した後、800~950℃の温度で2時間加熱後熱間圧延により6mm tの厚さに仕上げた。酸洗し表面のスケールを除去した後0.5mm tの厚さまで冷間圧延した。その後800~900℃の温度で5~10分間溶体化処理後水焼入れを行った。なお、この溶体化処理後の結晶粒度は10μmに調整した。そして0.3mm tまでの仕上げ冷間圧延後、400~500℃の温度で1~7時間の時効処理を最大強度が得られる条件で行い、最後は#1200エメリー紙により表面研磨し、スケール等の表面欠陥を除去し供試材とした。

【0017】

【表1】

| | | 化 学 组 成 (重量%) | | | | | | | |
|-----------------------|----|---------------|------|------|-------|--------|--------|------|--------------------------|
| | | Cu | Ni | Si | Mg | S | O | Zn | 副成分 |
| 本 発 明 合 金 | 1 | 残 | 2.25 | 0.55 | 0.026 | 0.0008 | 0.0007 | — | — |
| | 2 | 残 | 3.67 | 0.97 | 0.047 | 0.0010 | 0.0008 | — | Co : 0.23 |
| | 3 | 残 | 1.87 | 0.43 | 0.028 | 0.0010 | 0.0014 | — | Cr : 0.12, Zr : 0.09 |
| | 4 | 残 | 2.71 | 0.60 | 0.098 | 0.0004 | 0.0007 | — | Ti : 0.27, Al : 0.65 |
| | 5 | 残 | 3.50 | 0.80 | 0.049 | 0.0012 | 0.0012 | — | Sn : 0.35, P : 0.007 |
| | 6 | 残 | 0.84 | 0.19 | 0.050 | 0.0012 | 0.0014 | 7.30 | B : 0.008, Al : 0.60 |
| | 7 | 残 | 3.62 | 0.93 | 0.049 | 0.0011 | 0.0005 | 0.92 | — |
| | 8 | 残 | 1.41 | 0.35 | 0.085 | 0.0010 | 0.0013 | 9.80 | Fe : 0.34, Ti : 0.06 |
| | 9 | 残 | 2.85 | 0.75 | 0.067 | 0.0008 | 0.0006 | 1.82 | — |
| | 10 | 残 | 2.51 | 0.61 | 0.038 | 0.0011 | 0.0013 | 0.37 | In : 0.08, As : 0.007 |
| | 11 | 残 | 1.29 | 0.33 | 0.022 | 0.0005 | 0.0009 | 3.16 | Mn : 0.51 |

| | | | | | | | | | |
|------|----|---|------|------|-------|--------|--------|------|-------------------------|
| 比較合金 | 12 | 残 | 5.38 | 0.86 | 0.054 | 0.0007 | 0.0009 | — | — |
| | 13 | 残 | 3.10 | 1.13 | 0.092 | 0.0073 | 0.0013 | 1.54 | — |
| | 14 | 残 | 3.19 | 0.75 | 0.003 | 0.0005 | 0.0005 | 18.9 | Sn : 0.53, P : 0.024 |
| | 15 | 残 | 2.54 | 0.68 | 0.33 | 0.0006 | 0.0012 | 5.10 | — |
| | 16 | 残 | 0.38 | 0.12 | 0.015 | 0.0009 | 0.0026 | — | Cr : 0.13 |
| | 17 | 残 | 0.44 | 0.38 | 0.46 | 0.0012 | 0.0014 | — | Fe : 0.16, P : 0.031 |
| | 18 | 残 | 1.96 | 0.45 | 0.051 | 0.0025 | 0.0013 | 26.8 | — |
| | 19 | 残 | 2.89 | 0.69 | — | 0.0011 | 0.0014 | 7.43 | — |
| | 20 | 残 | 1.93 | 0.52 | 0.038 | 0.0032 | 0.0019 | 1.15 | Sn : 2.32 |
| | 21 | 残 | 1.40 | 0.08 | 0.076 | 0.0006 | 0.0008 | 1.42 | — |

【0018】供試材について引張強さ、伸び、導電率、応力緩和特性、錫めっき耐熱剥離性、銀めっき性、耐応力腐食割れ性を試験した。引張強さ、伸びはJIS13B引張試験片を用い引張試験を行い測定した。導電率は10mmw×100mm lの試験片に加工後四端子法により20℃にて電気抵抗を測定し、導電率に換算した。応力緩和特性は図1の様に10mmw×100mm lに加工した板厚0.3mmの試験片に標点距離l=50mmで高さ $y_0=20$ mmの曲げ応力を負荷し、150℃にて1000時間加熱後の図2に示す永久変形量(高さ)yを測定し応力緩和率 $\{[y(\text{mm})/y_0(\text{mm})] \times 100(\%) \}$ を算出した。錫めっき耐熱剥離性は供試材に0.5~0.8 μm の銅下地めっきを施した後、1~1.5 μm の錫を電気めっきした後加熱リフロー処理したものについて10mmw×100mm lに切断後150℃にて所定時間(100時間毎)加熱し、曲げ半径0.3mm(=板厚)で片側の90°曲げを往復1回行い、20倍の視野で表裏面の曲げ部近傍を観察しめっき剥離の有無を確認した。銀めっき性は供試材に銅フラ

ッシュめっきを下地として銀めっきを1 μm 施したものについて450℃で2分間加熱後1470mm²(7mm□×30個)の領域についてふくれの数を計測した。耐応力腐食割れ性は12.5mmw×150mm lに加工した供試材をループ状に固定したまま室内で12時間放置後、14%アンモニア水を2リットル含有する容積10リットルのデシケータ中に放置し、目視にて割れ発生の有無を調べ割れ発生までの時間にて評価した。耐マイグレーション性は供試材を10mmw×100mm lに加工し、図3のように2枚1組でセットし、図4の様に水道水(300ml)中に浸漬した。次にこれら2枚の供試材間に14Vの直流電圧を印加し、経過時間に対する電流値の変化を測定した。この結果の代表例を図5に示す。そして耐マイグレーション性の評価は電流値が1.0Aになるまでの時間(図5中矢印)で行った。これらの評価結果を表2に示す。

【0019】

【表2】

| | | 引張強 さ(N/ mm ²) | 伸び (%) | 導電 率(%) IACS | 応力 緩和 率(%) | 錫めっ き耐熱 剥離性 (hr) | 銀めっき 性(ふく れの数) | 耐応力 腐食割 れ性 (hr) | 耐マイグ レーション 性 (min) |
|----------|----|----------------------------------|-----------|--------------------|------------------|---------------------------|----------------------|--------------------------|-----------------------------|
| 比較 合金 | 1 | 683 | 7.9 | 49 | 16 | 600 | 0 | > 500 | 530 |
| | 2 | 741 | 5.3 | 41 | 15 | 500 | 0 | > 500 | 700 |
| | 3 | 675 | 8.9 | 49 | 16 | 700 | 0 | > 500 | 500 |
| | 4 | 717 | 6.3 | 42 | 10 | 600 | 0 | > 500 | 570 |
| | 5 | 724 | 5.2 | 37 | 15 | 500 | 0 | > 500 | 620 |
| | 6 | 534 | 13.3 | 40 | 16 | >1000 | 0 | 400 | 420 |
| | 7 | 716 | 6.5 | 45 | 14 | >1000 | 0 | > 500 | 720 |
| | 8 | 642 | 5.2 | 42 | 13 | >1000 | 0 | 400 | 600 |
| | 9 | 698 | 8.4 | 43 | 14 | >1000 | 0 | > 500 | 640 |
| | 10 | 698 | 7.8 | 45 | 16 | >1000 | 0 | > 500 | 570 |
| | 11 | 611 | 11.1 | 42 | 17 | >1000 | 0 | > 500 | 500 |
| 比較 合金 | 12 | 836 | 2.1 | 39 | 15 | >1000 | 0 | > 500 | 680 |
| | 13 | 704 | 6.6 | 29 | 21 | 100 | 67 | > 500 | 830 |
| | 14 | 735 | 4.4 | 23 | 24 | >1000 | 0 | 50 | 790 |
| | 15 | 691 | 4.6 | 41 | 9 | 100 | 0 | 400 | 690 |
| | 16 | 454 | 17.6 | 60 | 22 | 300 | 4 | > 500 | 350 |
| | 17 | 643 | 10.2 | 53 | 10 | 100 | 0 | > 500 | 470 |
| | 18 | 657 | 9.3 | 19 | 21 | >1000 | 3 | 10 | 800 |
| | 19 | 698 | 6.1 | 43 | 23 | >1000 | 0 | > 500 | 670 |
| | 20 | 729 | 5.9 | 37 | 24 | 400 | 10 | > 500 | 520 |
| | 21 | 480 | 22.8 | 52 | 11 | >1000 | 0 | > 500 | 200 |

【0020】この表から本発明合金は良好な強度、導電性を有し、応力緩和特性も良好であり、錫めっき耐熱剥

離性、銀めっき性といった表面品質も非常に良好であり、また耐応力腐食割れ性も良好であることがわかる。

【0021】これらに反し比較合金については、No. 12はNi量が高いため、強度は高いものの伸びが低く、加工性があまり良好ではない。No. 13はSi量、S量が高いため、導電性が低く、応力緩和特性も悪く、錫めっき耐熱剥離性、銀めっき性といった表面品質も悪い。No. 14はMg量が低く、Zn量が多い例であるが、Mg量が低いため応力緩和特性があまり良好ではなく、Zn量が多いため導電性が低く、耐応力腐食割れ性も悪い。No. 15、17はMg量が多い例だが、応力緩和特性は良好であるが、錫めっき耐熱剥離性が悪い。No. 16はNi量が低くO（酸素）量が高いため、十分な強度は得られず、応力緩和特性、錫めっき耐熱剥離性、銀めっき性が悪い。

【0022】No. 18はS量、Zn量が多いため、応力緩和特性、銀めっき性、耐応力腐食割れ性が悪い。No. 19はMgを添加しない例だが応力緩和特性があまり良好ではない。

【0023】No. 20はO、S量が高いため、応力緩和特性、錫めっき耐熱剥離性、銀めっき性が悪い。No. 21はSi量が少ないため、十分な強度が得られず、耐マイグレーション性も悪い。

【0024】以上説明したように本発明合金はCu-N

i-Si-Mg系合金のO、S量を規定し、Znを添加し、さらにP、B、As、Fe、Co、Cr、Al、Sn、Ti、Zr、In、Mnのうち1種又は2種以上を添加することにより、高強度、高導電でしかも応力緩和特性も良好で、めっき耐熱剥離性、銀めっき性も良好で耐応力腐食割れ性も良好なものである。

【0025】

【発明の効果】本発明合金は高強度、高導電で応力緩和特性、めっき耐熱剥離性、銀めっき性、耐応力腐食割れ性が良好な銅合金であって、コネクタ、リレー、スイッチ等広く電子部品分野で使用されるべき銅合金である。

【図面の簡単な説明】

【図1】応力緩和特性試験法の説明図である。

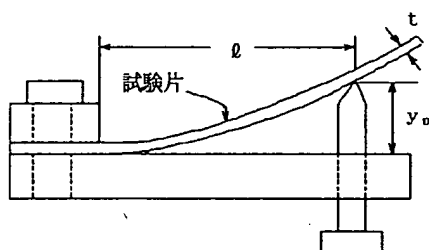
【図2】応力緩和特性試験の永久変形量についての説明図である。

【図3】耐マイグレーション性試験供試材の説明図である。

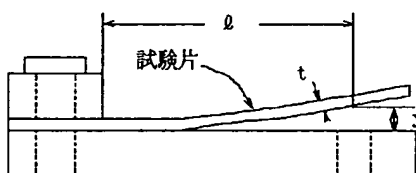
【図4】耐マイグレーション性試験の説明図である。

【図5】耐マイグレーション性試験における経過時間に対する電流値野変化を示すグラフである。

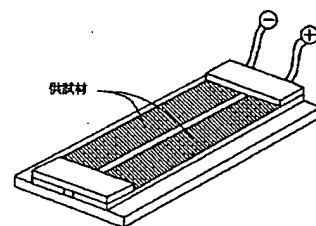
【図1】



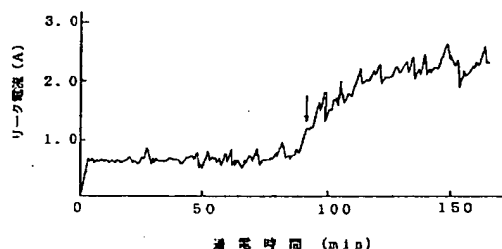
【図2】



【図3】



【図5】



【図4】

